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Abstract:

LEAD SLAG REDUCTION

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A process for lead slag reduction subjects the slag to top-submerged lance injection of oxygen containing gas and fuel, via a vertically suspended lance having its lower tip end submerged in the slag. The injection generates a combustion zone in the slag in which fuel is combusted and generates turbulent conditions forming a slag coating on the lower extent of the lance which is solidified by the cooling effect of the injected gas. The injection is conducted under reducing conditions, using a sulphidic material as a reductant, to reduce lead in the slag to metallic lead and thereby form a molten lead phase which is able to be tapped as lead bullion.

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Claims:

Claims

1. A process for lead slag reduction, wherein the slag is subjected to top submerged lance (TSL) injection of oxygen containing gas and fuel, via a vertically suspended lance having its lower tip end submerged in the slag, to generate a combustion zone in the slag in which fuel is combusted and to generate turbulent conditions forming a slag coating on the lower extent of the lance which is solidified by the cooling effect of the injected gas, and wherein the TSL injection is conducted under reducing conditions, using a sulphidic material as a reductant, to reduce lead in the slag to metallic lead and thereby form a molten lead phase which is able to be tapped as lead bullion.

2. The process of claim 1, wherein sulphidic material is selected from bulk concentrate, such as a bulk lead/zinc/silver concentrate, a lead or zinc concentrate, sulphidic drosses, pyrites, and mixtures of two or more of these materials.

3. The process of claim 1, wherein the sulphidic material is a lead concentrate.

4. The process of any one of claims 1 to 3, wherein the process is conducted substantially without use of carbonaceous reductant.

5. The process of any one of claims 1 to 3, wherein the process is conducted without use of carbonaceous material other than carbonaceous material present in the sulphide material.

6. The process of any one of claims 1 to 5, wherein lead sulphide concentrate is used as the sulphidic material reductant.

7. The process of any one of claims 1 to 6, wherein the process is conducted as a second stage following a TSL lead concentrate first stage smelting of a lead containing feed material to produce a lead product and a leadcontaining slag, and slag produced in the first stage is the slag lead containing slag for the second stage.

8. The process of claim 7, wherein the lead containing feed material to the first stage is at least one of lead concentrate, secondary lead sources including lead acid batteries, recycled lead containing metal.

9. The process of claim 7 or claim 8, wherein the stages are conducted in respective TSL furnaces.

10. The process of claim 7 or claim 8, wherein the stages are conducted batchwise in a single TSL furnace.

11. The process of any one of claims 7 to 10, wherein the second stage is followed by a third, slag fuming stage.

12. The process of claim 9, wherein the second stage is followed by a third, slag fuming stage conducted in the same furnace at the second stage.

13. The process of claim 10, wherein the second stage is followed by a third, slag fuming stage conducted in a second TSL furnace.

14. The process of claim 10 or claim 13, wherein on achieving a sufficient volume of slag produced in the first stage smelting, a change from the first to the second stage is made by: (i) continuing stop the feeding of lead sulphide concentrate following termination of the first stage; and (ii) reducing the oxygen content of the injected oxygencontaining gas from the level used in the first stage to the level suitable for the lower oxygen potential required in the second stage.

15. The process of any one of claims 7 to 14, wherein the first stage is conducted whereby oxygen is used as the driving force to convert lead sulphide into lead metal through the direct reaction: $PbS + O_{2(g)} \rightarrow Pb(l, + SO_2(g)$ (1) with the compefing reacfions: $PbS + O_{2(g)} PbO_{(l)} + SO'2(g)$ (2) $PbS \rightarrow PbS_{(g)}$ (3) $Pb_{(l)} \rightarrow Pb_{(g)}$ (5).

16. The process of any one of claims 7 to 15, wherein the second stage, is conducted at a temperature resulting in lead oxide in the slag being reduced by use of lead concentrate as the sulphidic material reductant, whereby the reactions involved at the temperature are: $2PbO(siag) + PbS \rightarrow 3Pb(i) + SO_{2(g)}$ K=26.7 (6) $2PbO(siag) + PbS \rightarrow 3Pb(g) + SO_2(g)$ K=1.2 x $10^{"6}$ (7) $2ZnO(siag) + PbS \rightarrow Pb(i) + 2Zn_0) + SO_{2(g)}$ K=3.4 x $10^{"7}$ (8) $2ZnO(siag) + PbS \rightarrow Pb(i) + 2Zn_{(g)} + SO_2(g)$ K=4.5 x $10^{"6}$ (9).

17. The process of any one of claims 7 to 16, wherein the second stage is conducted at a temperature in the range of 1200^0C to 1250^0C.

18. The process of any one of claims 7 to 17, wherein the first stage is conducted at a temperature in the range of 950^0C to 1200^0C.

Description:

LEAD SLAG REDUCTION

This invention relates to a process for lead slag reduction, utilising top-submerged lance injection.

Top-submerged lance (TSL) injecfion was developed in the early 1970's. Since then, the technology has become widely adopted for new startup plants for processing a range of non-ferrous, ferrous and waste materials.

The TSL technology utilises a bath smelting system in which a vertically suspended lance has its lower tip submerged in molten slag layer of the bath contained in a suitable furnace. Process gases, such as air or air and oxygen, and fuel are injected through the lance into the slag. The fuel is combusted

at the lance tip to provide heat to the furnace. The injection generates turbulence in, and splashing of, the slag such that the slag is thoroughly mixed. Controlled swirling of the process gas as it flows through the lance cools the lance outer surface sufficiently to solidify slag splashed onto the lance and form a slag layer which protects the lance in the highly aggressive furnace environment.

The TSL bath smelting system utilises reactions between sulphidic, oxidic and/or metallic components in the slag or provided as feed to the bath, and contained oxygen and ferric oxide in the bath. Critical process phenomena including feed material dissolution, energy transfer, reaction and primary combustion, all take place in the slag layer. The intense agitation of the slag resulting from the submerged injection through the lance ensures that reactions occur rapidly and residence times are low.

The degree of process oxidation and reduction is able to be controlled by adjusting the ratio of fuel to oxygen supplied to and through the lance, and by the proportion of reductant to feed. The furnace is able to be operated through a range of conditions from strongly oxidising to strongly reducing conditions.

TSL technology has been used to smelt lead concentrates and secondary feeds at a temperature of from about 950 ^{0} C to 1200 ^{0} C, preferably in the range of 1000 ^{0} C to 1 100 ^{0} C, to directly produce lead bullion and a lead rich slag, such as a slag having from 30 to 50 wt% lead. The lead bullion, such as with about 98 wt% lead, is tapped periodically from the furnace during smelting, for transfer to a lead refinery. The slag remaining is subjected to a lead reduction operation, to recover further lead and produce a discardable low lead slag. The smelting also produces a lead fume product which is returned to a subsequent smelting cycle to maximise recovery of lead to bullion.

In some instances, the high lead slag produced by such use of the TSL technology has been sent to a blast furnace for reduction and further recovery of lead bullion. The slag from the blast furnace then has been sent to a slag fumer for recovery of zinc as fume. In other instances, the high lead slag has been subjected to reduction and fuming stages by further application of TSL technology.

The TSL processing of the high lead slag resulting from smelting has been conducted as second and third stages of reduction and fuming, respectively, using the same reactor as used for the first stage of smelting, in a three stage batch process. In an alternative, the high lead slag has been tapped periodically from a continuous TSL smelting furnace, and transferred to a second furnace in which the slag is subjected to a reduction stage and, optionally, to a fuming stage. In each case, the reduction stage is operated with a lower oxygen potential and a higher temperature, such as about 1250 ^{0} C, than used in the smelting stage. Lead is recovered from the slag during the reduction stage as bullion which is tapped for downstream refining. A lead fume product from the reduction stage is recycled to the smelting stage

to maximise recovery of lead to bullion. A resultant low lead slag, such as with about 5% lead, can be tapped and processed separately, or it can undergo a TSL fuming step to clean the slag and maximise metal recovery.

The TSL slag fuming stage uses a more strongly reducing furnace environment than the reduction stage. The intense bath turbulence and gas

dynamics of the TSL operation are used to remove much of the remaining lead and zinc as fume, leaving a slag suitable for discard, such as with about 0.5 wt% lead and about 3 wt% zinc. When lead concentrates have been smelted, the slag from the reduction stage will usually contain significant levels of zinc, in which case the fume product from the fuming stage is high in zinc oxide, such as from about 50 to 70 wt% zinc. This fume is not suitable for recycling to the smelting stage, but needs to be removed from the system for separate processing to recover the zinc and lead.

The present invention provides an improved process for the reduction of a lead containing slag. The slag may be that resulting from the TSL smelting of a lead source material, such as at least one of lead concentrate, secondary lead sources including lead acid batteries, and recycled lead containing metal. However, the invention also can be applied to a suitable lead containing slag from another source, such as another bath smelting process. Also, while the lead content of slag from TSL smelting of a lead concentrate may be in the range of 40 to 50 wt%, slag with a lower or higher lead content can be used in the process of the present invention. Indeed, at the lower end, the lead content need only be at a level sufficient to warrant reducing the slag to achieve a level of about 5 wt% lead in the slag.

Traditional processing of lead via pyrometallurgical routes has involved the reduction of high lead slags by carbonaceous materials, using a range of apparatus types. Lead blast furnaces typically utilise relatively expensive coke as carbonaceous reductant. Modern bath smelting technologies, such as TSL technology, employ coal, a cheaper carbonaceous reductant. We have found that unexpected benefits are able to be obtained from use of an alternative reductant, instead of coal or other carbonaceous reductant, in slag reduction using TSL technology.

According to the present invention, there is provided a process for lead slag reduction, wherein the slag is subjected to top-submerged lance injection of oxygen containing gas and fuel, via a vertically suspended lance having its lower tip end submerged in the slag, to generate a combustion zone in the slag

in which fuel is combusted and to generate turbulent conditions forming a slag coating on the lower extent of the lance which is solidified by the cooling effect of the injected gas. The TSL injection is conducted under reducing conditions, using a sulphidic material as a reductant, to reduce lead in the slag to metallic lead and thereby form a molten lead phase which is tapped as lead bullion.

The sulphidic material may be any sulphide containing material which is compatible with the process of lead recovery by lead slag reduction. The sulphidic material may be a bulk concentrate, such as a bulk lead/zinc/silver concentrate, a lead or zinc concentrate, sulphidic drosses, pyrites, or a mixture of two or more such materials. The sulphidic material preferably is a lead concentrate, such as that smelted in generating the slag to be subjected to the lead slag reduction of the invention.

The process of the present invention obviates the need for use of carbonaceous reductant. While a minor proportion of carbonaceous reductant can be tolerated, this is not desirable as it partially reduces the benefits obtainable with use of sulphidic material alone as reductant. Also, some concentrates contain a proportion of carbonaceous material, such as graphite, and an increase in that proportion is not desirable.

In obviating the need for carbonaceous reductant, the use of sulphidic material as reductant reduces greenhouse gas emissions. That is, generation of CO and CO_2 is substantially avoided, although some small quantity of CO_2 may result to the extent that the sulphidic material contains oxidation product such as lead carbonate and graphitic materials.

The use of sulphidic material as reductant of course results in generation of SO_2. However, as will be appreciated, the SO_2 content of furnace off-gases are able to be recovered and utilised, such as in the production of sulphuric acid.

The present invention, as illustrated later herein, also has further practical benefits. The use of a sulphidic material reductant surprisingly

enables a better separation of lead and zinc, to give more efficient processing.

Also, the sulphidic material reductant results in higher productivity of lead per smelt/reduction cycle where the sulphidic material contains lead.

Particularly with the use of lead sulphide concentrate as the sulphidic material reductant, the lead slag reduction process of the present invention is well suited for use as a second stage following a TSL lead concentrate first stage smelting of a lead containing feed material. Such a second stage may be conducted in a separate furnace rather than the same furnace used for the first stage smelting. However, there are particular benefits in conducting the two stages (and optionally a third stage of slag fuming) in the one furnace. Thus, on achieving a sufficient volume of slag produced in the first stage smelting, it is necessary only to:
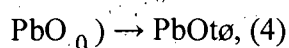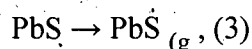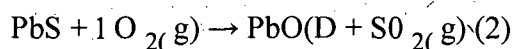
(i) continue rather than stop the feeding of lead sulphide concentrate following termination of the first stage; and

(ii) reduce the oxygen content of the injected oxygen-containing gas from the level used in the first stage to the level suitable for the lower oxygen

potential required in the second stage.

In the first stage (whether in the same or a different furnace used for the second stage), oxygen is used as the driving force to convert lead sulphide into lead metal through the direct reaction:
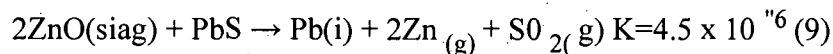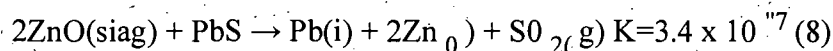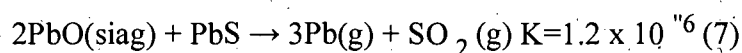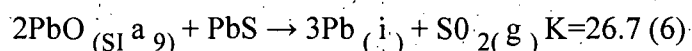
$$PbS + O_2 (g) \rightarrow Pb(i) + SO_2 (g) \quad (1)$$

with the competing reactions:

$$PbS + 1O_{2(} g) \rightarrow PbO(D + SO_{2(} g) \quad (2)$$

$$PbS \rightarrow PbS_{(g}, \quad (3)$$

$$PbO_{0)} \rightarrow PbOt\o, \quad (4)$$

In this Pb-S-O system, the lead can report to any of the metal, slag or fume phases.

In the second, slag reduction stage, lead oxide in the slag is reduced by sulphidic material reductant. The following equations, for use of lead concentrate as the sulphidic material reductant, describe the reactions involved at $1200\ ^0$ C:

$$2PbO_{(SI} a_{9)} + PbS \rightarrow 3Pb_{(i)} + SO_{2(} g_{)} \quad K=26.7 \quad (6)$$

$$2PbO(siag) + PbS \rightarrow 3Pb(g) + SO_2 (g) \quad K=1.2 \times 10^{"6} \quad (7)$$

$$2ZnO(siag) + PbS \rightarrow Pb(i) + 2Zn_{0)} + SO_{2(} g) \quad K=3.4 \times 10^{"7} \quad (8)$$

$$2ZnO(siag) + PbS \rightarrow Pb(i) + 2Zn_{(g)} + SO_{2(} g) \quad K=4.5 \times 10^{"6} \quad (9)$$

From equations (6) to (9) it can be determined that, by using lead sulphide such as lead sulphide concentrate to carry out the reduction, the equilibria favour the deportment of lead to the molten bullion phase and zinc to the slag as zinc oxide. This enhances the separation between the lead and zinc so that lead can be removed during the reduction stage, maximising the retention of zinc in the slag for subsequent fuming. We have found that a key to this slag reduction stage is the degree to which lead can be reduced from the slag by lead sulphide before sulphur accumulates in the bullion. We have found that lead levels in slag down to about 5% lead are achievable before the level of sulphur dioxide in the furnace offgas begins to diminish, indicating that reaction (6) was substantially reduced or no longer is effective.

In order that the invention may more readily be understood, reference now is directed to the accompanying drawings, in which:

Figure 1 is a perspective view, partly cut away, illustrating a TSL furnace suitable for use in the present invention;

Figure 2 shows a flowsheet for a prior art three stage process for TSL recovery of lead from lead sulphide concentrates;

Figure 3 shows a flow chart for a three stage process according to the present invention for TSL recovery of lead from lead sulphide concentrates;

Figure 4 is a schematic flowsheet for a multi-furnace process corresponding to the process of Figure 3;

Figure 5 shows an alternative flowsheet to that of Figure 4.

Figure 6 shows a theoretical distribution of lead between slag, metal and fume under equilibrium conditions for the first stage of a process as illustrated by each of Figures 2 to 5; and

Figure 7 illustrates a control chart for lead and zinc for a typical operation in a process according to the invention corresponding to the flow chart of Figure 3.

Figure 1 shows a TSL furnace 10 suitable for use in the present invention but which is shown partly cut-away to reveal its interior. The furnace 10 has a cylindrical lower portion 12 for containing a molten bath 14 comprising slag, or having an upper layer of slag. Extending from the upper extent of lower portion 12, the furnace 10 has an asymmetrical, frnsto-conical roof portion 16 and, above portion 16, an off-take flue 18. The portions 12 and 16 of furnace 10 typically have an outer shell 20 of steel which is lined with suitable refractory 22.

A vertically suspended lance 24 extends to the furnace 10, close to the axis of portion 12. The lance 24 passes through the roof portion 16 and is able to be raised or lowered by a carriage (not shown) to which the upper end of lance 24 is connected. The carriage is moveable vertically on a guide strncture (also

not shown). By means of lance 24, an oxygen-containing gas and a suitable fuel is able to be injected into the bath 14. Also, feed materials are able to be charged to the furnace 10, to fall into the bath 14, via inlet port 26. Means (not shown) are provided for substantially sealing around the opening in furnace portion 16 through which lance 24 passes, and at port 26. Also, furnace 10 is kept below atmospheric pressure to prevent gases from exiting from the furnace 10 other than via flue 18.

The lance 24 in the arrangement illustrated comprises a concentric arrangement of an outer tube 27, an interrnediate tube 28 and an inner tube

29. The outer tube 27 tenninates a substantial distance above the lower, tip end of lance 24 and above the bath 14. The tubes 28 and 29 are substantially the same length. The process gas which provides cooling for the outer

surface of intermediate tube 28 is able to be supplied via a conduit 30 to the annular space between tubes 27 and 28. An oxygen containing gas is able to be supplied via a conduit 31 to the annular space between tubes 28 and 29. Fuel is able to be supplied via a conduit 32 to the bore of tube 29. While not shown, a swirler device is provided in the space between tubes 28 and 29 adjacent to the lower tip end of lance 24, to impart a helical flow to the oxygen-containing gas and thereby enhance mixing of that gas and the fuel at the tip of lance 24.

The fuel may be entrained in a carrier gas if it is a solid such as fine particulate coal. However, the fuel also may be a suitable hydrocarbon gas or liquid.

On start-up with furnace 10, the lance 24 is lowered to a position in which its lower tip end is above the initially quiescent bath 14. With the supply of oxygen-containing gas via conduit 31 and fuel via conduit 32, the lance 24 is fired by igniting the resultant mixture of oxygen-containing gas and fuel issuing from the lower, tip end of the lance. The materials supplied through the lance for this combustion of the fuel are supplied at a high velocity which results in generation of a very strong jet and splashing of the slag of bath 14. The external surface of tube 28 below the lower end of tube 27 becomes covered with molten slag which is solidified to form a protective coating 34 (see enlarged insert A) by cooling of tube 28 by the oxygen-containing gas. If not previously commenced, a flow of the cooling gas via conduit 30 is commenced,

with that gas issuing from the lower end of tube 27 to further cool the tube 28.

The lance 24 then is lowered so that its lower, tip end is submerged in the slag, to provide ongoing submerged injection and combustion of fuel within the slag. The top-submerged injection generates substantial turbulence in the slag such that splashing of the slag continues, and intimate mixing of feed to the slag is able to be achieved. The furnace then is in a condition enabling a required pyrometallurgical process to be conducted. In the course of that process, a cooling gas can be supplied via conduit 30 to the space between tubes 27 and 28 so as to issue into a gas space 36 above the bath 14. The cooling gas further assists in cooling of the outer surface of tube 28 and maintenance of solid slag coating 34. The cooling gas may be a non-oxidising gas such as nitrogen, or it may be an oxygen-containing gas such as air.

Turning now to Figure 2, the flowsheet shown illustrates a three stage process for recovery of lead from lead source material by TSL technology. The process has a SMELT stage, followed by a REDUCTION stage and finally by a

FUMING stage. In the first, SMELT stage, the lead source material such as lead concentrate is smelted in a TSL furnace, such as a furnace 10 as shown in Figure 1. In the TSL furnace, the source material and flux material are fed to a slag bath and smelted by top-submerged lance injection of an

oxygen containing gas and fuel, to generate turbulence in the slag and combustion of a mixture of the fuel and oxygen-containing gas.

In the SMELT stage, the lead source material is fed together with lead recycle streams. These streams include lead-rich fume from the smelting and from the REDUCTION stage, and lead residues from the separate processing of zinc- rich fume from the FUMING stage. However, in addition to lead concentrate, the lead source material may include secondary lead sources including lead acid batteries and/or recycled lead containing metal. The SMELT stage is conducted under slightly oxidising conditions, at a temperature in the range of $950\,^0\mathrm{C}$ to $1200\,^0\mathrm{C}$, preferably $1000\,^0\mathrm{C}$ to $1100\,^0\mathrm{C}$ which depends on slag chemistry and on the grade of the source material.

Apart from lead-rich fume, the SMELT stage produces lead bullion and a slag having a high content of lead, as lead oxide. Thus, smelting is conducted in the presence of slag forming fluxes. The recycle streams help to maximise the lead content of the feed streams and so increase the amount of lead reporting to the bullion.

The bullion is tapped periodically from the furnace and despatched for refining. The lead rich fume is collected and recycled to the SMELT stage. The high lead slag, with for example approximately 30 to 50 wt% lead, is tapped when the smelting furnace reaches capacity. However, the slag either remains in the furnace used for smelting to enable further recovery of lead in the REDUCTION stage prior to tapping, or it is transferred, preferably while still in a molten state, to a second TSL furnace, also such as shown in Figure 1 in which the REDUCTION stage is conducted.

The REDUCTION stage involves recovery of lead contained in the high lead slag from the SMELT stage, by top-submerged injection. For this, a reducing condition is maintained in the furnace by the addition of reductant coal and control of the lance injection conditions, specifically the oxygen to fuel ratio. The conditions result in reduction of lead oxide to metallic lead, to produce lead bullion, and leave a slag with a lower level of lead, for example about 5% lead. The lower level of lead in the slag requires that the slag reduction be carried out at a higher temperature, for example in the range $1200\,^0\mathrm{C}$ to $1250\,^0\mathrm{C}$, due to the increasing slag liquidus temperature.

The products of the REDUCTION stage are lead bullion, a lead rich fume and a slag containing for example approximately 5% lead and a substantially higher level of zinc. The bullion is tapped and despatched for refining. The lead-rich fume is collected and recycled to the SMELTING stage to maximise direct recovery of lead to bullion. The high zinc slag, if not tapped from the furnace, stockpiled and processed separately, is left in the REDUCTION stage TSL furnace, or transferred to a further TSL or other furnace, for final recovery of metal values.

The FUMING stage recovers the last metal values to oxide and produces a slag suitable for disposal or for use as, for example, a building material, slag

cement or road building. To recover the metal values, the process operating temperature is increased to about 1300 ^{0} C. The supply of reductant coal is continued from the previous REDUCTION stage and is added to the slag to produce a more strongly reducing bath condition. The coal rate is controlled to generate an oxygen potential which is sufficiently low, for example about 10 $^{"8}$ atmospheres, to promote fuming of the volatile lead and zinc. These metals then are oxidised above the bath and the resultant fume is collected in a gas handling system associated with the furnace. Oxygen for oxidation of the lead and zinc vapours may be supplied to the furnace by the lance used for top submerged injection, such as via tube 27 in the case of a lance 24 as shown in Figure 1. However the oxygen alternatively may be supplied above the bath by an alternative device.

The process illustrated in Figure 3, in broad overall form, is similar to that described with reference to Figure 2. Thus, description of Figure 3 will be limited to matters of difference. A principal and important difference is that the REDUCTION stage is conducted in accordance with the present invention.

The REDUCTION stage again requires that a reducing condition is maintained in the TSL furnace by the addition of reductant and control of lance injection conditions, specifically the oxygen to fuel ratio. However, rather than use a carbonaceous reductant such as coal, a sulphidic material, such as detailed earlier herein but preferably lead sulphide concentrate is charged to the bath and reduces the lead oxide of the slag by the reactions of equations (6) to (9) detailed above.

Thus, if the REDUCTION stage is in the same TSL furnace as used for a SMELT stage for lead source material comprising lead sulphide concentrate alone, the feeding of lead sulphide is able to be continued through these two successive stages. The transition between the stages is not marked by the cessation of feeding source material and the commencement of feeding of a different reductant material to the TSL furnace (as with the commencement of

feeding reductant coal on cessation of feeding lead source material in the process of Figure 2). Rather, that transition is marked by a continuation of feeding source material and, without adding carbonaceous reduction, changing conditions such that, instead of the lead sulphide source material being oxidised to increase the lead content of the slag as in the SMELT stage, the source material in the REDUCTION stage reduces lead oxide in the slag to metallic lead which reports substantially to bullion. The change in conditions is achieved by ceasing the addition of oxygen for sulphide smelting reactions as well as reducing the ratio of oxygen to fuel that is supplied by top-submerged injection. At the same time the rate of addition of fuel is increased to raise the bath temperature from 950 ^{0} C to 1200 ^{0} C, preferably in the range 1000°C to 1100 ^{0} C in the SMELT stage to the range of 1200 ^{0} C to 1250 ^{0} C in the REDUCTION stage.

The REDUCTION stage of Figure 3, relative to that stage of Figure 2,

reduces greenhouse gas emissions by substantial avoidance of added carbonaceous reductant, such as coal, in the REDUCTION stage and hence by less reliance in the overall three stage process on carbonaceous reductant. Thus, carbon dioxide generation in the REDUCTION stage is substantially reduced, and occurs only to an extent determined by any carbonaceous content of the lead concentrate and the combustion of fuel. Also, again in the overall process of Figure 3, better separation of lead and zinc allows more efficient processing, while less dilution of feeds produces a higher direct recovery of lead. Additionally, use of lead sulphide as reductant results in the generation of sulphur dioxide, and sulphur in the offgas can be used to monitor the progress of the reactions of equations (6) to (9). Also, the lower tenor sulphur dioxide offgas produced in the REDUCTION stage according to the invention can be treated for sulphur dioxide recovery if not required to report directly to an acid plant.

It is found that, in the REDUCTION stage of Figure 3, the level of lead in the slag can be reduced to a suitable level before sulphur accumulates in the bullion to an unacceptable level. Thus, for example, the level of lead in the slag can be reduced at least to about 5% before the level of sulphur dioxide in

the offgas began to diminish, indicating that the reaction of equation (6) had ceased to be effective.

With the process of the present invention being used in the reduction stage of a three stage process, the use of a single TSL furnace for all three stages is suitable for small annual tonnages. However, because of the level of recycling, such an operation requires sufficient holding capacity to incorporate fume produced during the slag reduction stage and the fume produced in the slag fume stage.

A two furnace operation is suitable for medium size installations. In the example shown in Figure 4, TSL furnace A is used for the smelt stage, while TSL furnace B is used for the reduction and fume stages. In this configuration, furnace A can be operated in a continuous smelt mode with continual removal of lead and, once the furnace capacity has been reached, periodic tapping of slag. The slag tapped from furnace A is transferred to furnace B where the slag reduction stage is conducted as a batch operation. Once that batch operation has been completed and the resultant lead bullion has been tapped, the final slag cleaning of the fuming stage commences as the second batch operation in furnace B.

In Figure 4, the reference numerals for each of TSL furnaces A and B indicate the same features as for furnace 10 shown in Figure 1. For furnace B, the "REDUCTANT" may be lead sulphide concentrate for the first batch operation of slag reduction for lead recovery, and carbonaceous reductant (preferably coal) for the second batch operation of slag fuming for zinc recovery. Continuous procedures are shown by solid lines, while batch process procedures are shown by broken lines.

Operation during the three stages with the arrangement illustrated by Figure

4 will be understood by the preceding description. However, Figure 4 also illustrates suitable offgas processing. For furnace A, the offgases pass to a cooling unit 40 in which heat energy is extracted. From unit 40, the gases pass to unit 42 for cleaning for removal of particulates, to collect lead rich

fumes. After unit 42, the gases pass to unit 44 in which sulphur is captured.

Finally, the gases pass to a stack 46 for discharge. For furnace B the processing for offgases from the slag reduction stage is shown in solid line, while that for the fuming stage is shown in broken line. In each case, the offgases are cooled in unit 50 and cleaned in unit 52. Lead rich fume is recovered from unit 52 during slag reduction by lead sulphide concentrate, while zinc rich fume is recovered from unit 52 during the slag fume stage. In the slag reduction stage, the gases from unit 52 pass to unit 44 for sulphur capture, and then to stack 46. However, in the fuming stage, the gases from unit 52 pass direct to stack 46 as they are substantially free of sulphur dioxide.

The lead rich fume recovered from units 42 and 52 is recycled to furnace A.

An alternative two furnace system is that shown in Figure 5. In this example both the smelt and reduction stages are conducted in Furnace A with Furnace B utilised for zinc removal in the furning stage. The overall operation with the system of Figure 5 readily will be understood from the description of the system of Figure 4. Further description therefore will be limited to matters in which the system of Figure 5 differs from that of Figure 4.

In Figure 5, the smelting stage and the slag reduction stage are conducted as successive batch operations in Furnace A. The slag tapped from furnace A at the end of the slag reduction stage is transferred to furnace B for final slag cleaning by the fuming stage. In the smelting stage lead sulphide concentrate (with secondaries, reverts, recycles) and fluxes are charged to furnace A, and smelted. At the end of the smelting stage, the changes for slag reduction are adopted. For this, the feeding of lead sulphidic concentrate and fluxes is continued, while the secondaries, reverts and recycles are discontinued. Also the oxygen content of the injected gas is adjusted to achieve the lower oxygen potential required during the slag reduction stage. During each of the smelting and slag reduction stages, offgases pass to cooling unit 40 and then to unit 42 for cleaning and removal of particulates, to collect respective lead rich fumes. For each of the smelting and reduction stages, the gases then pass to unit 44 for sulphure capture, and then to stack 46. During the slag fume stage, the

offgases pass to unit 50 for cooling, then to unit 52 for recovery of zinc rich fume, and then to stack 46 without the need for sulphur capture.

The lead rich fume recovered by unit 42 during the smelting stage, as well as the lead rich fume recovered by unit 42 during the slag reduction stage, is recycled to a further smelting stage in Furnace A.

For a large-scale installation, a three furnace configuration using three TSL furnaces can be employed. Each of the three stages is able to be carried out continuously in a respective furnace. Liquid slag flows continuously via a weir and launder from the smelt stage furnace to the slag reduction stage furnace, and similarly from the latter furnace to the fume stage furnace. Lead bullion is removed from the smelting and slag reduction furnaces. The final discard slag from the fume furnace may be continuously tapped through a weir for disposal.

With reference to Figure 6, there is shown a theoretical distribution of lead in the smelt stage of a process as illustrated in each of Figures 2 to 5, under equilibrium conditions using HSC Chemistry for Windows 5.1 (chemical reaction and equilibrium software available from SGE Software at www.sge.com). The data of Figure 6 is for a typical set of conditions for a given smelter and for one specific lead sulphide concentrate. Figure 6 shows the weight percent distribution of lead between slag, lead bullion and fume under those conditions, plotted against the volume of lance injected oxygen containing gas (at a given oxygen content) expressed in normal cubic metres per tonne of concentrate.

Figure 6 shows that the smelt stage is sensitive to the amount of lance injected oxygen containing gas. In the case illustrated, a difference of 50 Nm^3 per tonne of concentrate can mean the difference between 65% to 70% direct lead metal recovery.

The equilibrium case illustrated by Figure 6 assumes substantially complete mixing of the slag, lead source material and top-submerged injected oxygen- containing gas. While that injection achieves a high level of turbulence in the

slag, the bath is not at equilibrium as predicted by the model. There are a number of factors contributing to this, including:

(a) Injected gases contact only a small proportion of the total volume of the slag, and oxygen transfer throughout that volume is reliant on the Fe^2 VFe $^{3+}$ redox couple to transfer oxygen from the injected gases to molten lead source material taken up in the slag.

(b) It has been found that faster mixing is achieved above the lance tip relative to mixing below that tip. Substantially complete mixing in slag above the tip may be achieved in about 2 minutes for example, whereas mixing below the tip may require up to about 20 minutes.

(c) If the lead sulphide concentrate and flux material are mixed or pugged, as is preferred, then as the pug falls into the bath and is heated up there is opportunity for solids to react with each other before they are dispersed in the slag and melted. The solids are in contact with gases, evolved from moisture and generated by smelting reactions before contact with oxygen-containing gas. As a consequence, the proportion of lead lost to fume may be less than would be the case under the equilibrium condition. (d) Lead

sulphide concentrates can be quite variable, including with respect to any graphitic carbon content. A large proportion of the oxygen demand during smelting can be due to this carbon source. Variations in the graphitic carbon content of the lead source material, such as by about 4 to 10 wt%, can impact on the ability to optimise control of the process with respect to oxygen.

However, despite these factors, Figure 6 is indicative of the general level of distribution of lead in the smelt stage between slag, lead bullion and fume. Direct lead recovery in that stage is able to be optimised at, for example, about 65 to 70%. Lead recovery in the overall three stage process is able to be stabilised at about 95%, with the use of a sulphidic material such as lead sulphide concentrate as reductant in the reduction stage being comparable to the prior art practice based on the use of a carbonaceous reductant such as

coal. The remaining 5% lead is accounted for by lead in zinc rich fume produced in the fume stage and lead losses in discard slag from that stage.

Figure 7 shows the effectiveness of, and benefits from, the use of a sulphidic material such as lead sulphide concentrate as reductant in the reduction stage. Figure 7 is a control chart showing the weight percentage of each of lead and zinc in the slag after successive time intervals during successive smelt, reduction and fume stages of a three stage process conducted in a single TSL fumace.

In the period of the reduction stage of the process illustrated by Figure 7, the level of lead in the slag can be seen to drop rapidly, with the use of a sulphidic material, in this case a lead sulphide concentrate, as reductant adding to the quantity of zinc in the slag. This difference in reporting of lead and zinc, that is recovery of lead as bullion while the slag substantially retains and takes up further zinc, occurs to a significantly greater extent than when a carbonaceous reductant is used in the reduction stage. This results in a better separation of lead and zinc, with both the fume produced in the reduction stage being richer in lead and the fume produced in the fume stage being richer in zinc.

Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the constmctions and arrangements of parts previously described without departing from the spirit or ambit of the invention. An example of such a modification may be through the use of other sulphide bearing materials as the reductant, such as bulk concentrates, sulphide drosses and pyrites.

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